# THE REACTION OF $CH_2OO$ WITH $HNO_3$ INVESTIGATED WITH A STEP-SCAN FTIR SPECTROMETER

CHEN-AN CHUNG, CHO-WEI HSU, YUAN-PERN LEE, *Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan*.

Carbonyl oxides, which are known as Criegee intermediates, are important intermediates produced in ozonolysis of unsaturated hydrocarbons.[a] Criegee intermediates react readily with other atmospheric species such as $HNO_3$, $SO_2$, $(H_2O)_2$ and HCOOH, leading to production of OH, aerosols and organic acids in the atmosphere. The reaction coefficient between $CH_2OO$ and $HNO_3$ was reported to be $5.4\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. [b] Theoretical calculations also predict a similar rate coefficient for $CH_2OO$ + $HNO_3$, the reaction goes through a barrierless path to form nitrooxymethyl hydroperoxide (NMHP, $NO_3CH_2OOH$). Besides, due to large exothermicity(-184.9 kJ mol$^{-1}$), internally excited NMHP might decompose further to $CH_2ONO_3$ and OH.[c]

In this work, we utilized a step-scan FTIR coupled with a multipass White cell to record time-resolved IR absorption spectra of the reactants and products during the reaction of $CH_2OO$ with $HNO_3$ in a flow system with total pressure about 10 Torr. $CH_2OO$ was produced from the reaction of $CH_2I$ + $O_2$; $CH_2I$ was produced from photolysis of $CH_2I_2$ at 308 nm.[d] The IR absorption spectra were recorded at instrumental resolution 0.3 $cm^{-1}$. Newly observed bands at 825, 967, 1053, 1294, 1348, 1424, 1686 and 3587 $cm^{-1}$can be assigned to NMHP. The observed wavenumbers and relative intensities agree with the anharmonic vibrational wavenumbers and IR intensities predicted with the B3LYP/aug-cc-pVTZ method. In addition, we also observed several bands with clear rotational structure, which can be assigned to the absorption of $NO_2$, $H_2CO$ and $HO_2$. Observation of these species indicates that another decomposition route for excited NMHP might exist. Furthermore, absorption bands of unternally excited $HNO_3$ was also observed at low pressure, indicating that decomposition of pre-reaction complex can excite $HNO_3$. By probing the formation of NMHP and $NO_2$, the rate coefficient of this reaction was determined to be $(5.3\pm0.8)\times10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

[a] R. Criegee, Angew. Chem. Int. Edit. 14, 745 (1975).
[b] E. S. Foreman, K. M. Kapnas and C. Murray, Angew. Chem. Int. Edit. 55, 10419 (2016).
[c] P. Raghunath, Y. P. Lee and M. C. Lin, J. Phys. Chem. A 121, 3871 (2017).
[d] O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu,C. J. Percival, D. E. Shallcross and C. A. Taatjes, Science 335, 204 (2012).